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Berg, Rolf W.; Otero, Amalia Dopazo

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Analysis of adipate ester contents in poly(vinyl chloride) plastics by means of FT-Raman spectroscopy

R.W. Berg^{a,*}, Amalia Dopazo Otero^{a,b}

^a Department of Chemistry, The Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Lyngby, Denmark

^b Escuela Técnica Superior de Ingeniería, Universidad de Santiago de Compostela, Santiago de Compostela 15782, Spain

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Abstract

Fourier transform (FT-) Raman spectroscopy excited with a 1064 nm laser can be used to determine the content of plasticizers in commercial flexible poly vinyl chloride (PVC) products. Our previous study [T. Nørbygaard, R.W. Berg, Analysis of phthalate ester content in PVC plastics by means of FT-Raman Spectroscopy, *Appl. Spectrosc.* 58 (4) (2004) 410–413]—on detection of the presence of phthalate esters in PVC by FT-Raman spectroscopy—is here extended to the similar case of adipate esters (AEs) in samples of soft poly vinyl chloride plastics. Spectra of a range of adipate ester plasticizers (11 AEs) in pure form are reported. We studied if qualitative and quantitative determination of the adipate ester content would be possible based on the use of proper reference samples. It was found that AEs as a group cannot be definitively identified by their characteristic Raman bands because other aliphatic dicarboxylic esters have very similar bands. This limits the detection as to what kind of ester and how much is present in a sample. An essential finding was however that one can use the absence of any Raman band in the 1020–1060 cm^{−1} range of the adipate esters, as a means to verify that a given soft PVC plastics sample does not contain significant amounts of phthalate esters because these plasticizers do have strong bands at around 1060 cm^{−1}. Furthermore it must be remembered that bands may occur at around 1040 cm^{−1} in a PVC sample for other reasons than phthalate ester content.

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1. Introduction

Synthetic plastics and polymers are among the greatest inventions of the 20th century and have become some of the most important and widely-used materials. Many such products need to be soft and flexible so that they can take on different shapes and forms depending on their application. This is particularly true of poly vinyl chloride (PVC or [CH₂–CHCl]_n), which is often ‘plasticized’ or softened by use of compounds such as phthalate, adipate, trimellitate, benzoate and citrate esters and other compounds. More than 95% of the plasticizer production is for PVC end-use. Importantly, the plasticizers are not just additives, like fillers or pigments, but are major components that determine the physical properties of the

polymer products. More than 300 different types of plasticizers are known, of which between 50 and 100 are in commercial use.

PVC is readily distinguished from other common polymers (e.g. polyethylene, polypropylene, polystyrene) by the use of Raman spectroscopy. For comprehensive reviews on general application of Raman spectroscopy on polymers, e.g. publications by Everall [2] and Hendra and Maddams [3] should be consulted. A recent book by Hummel [4] gives an overview of plastic additive analysis by spectroscopic methods (mainly IR spectroscopy).

PVC is the best material for making plastic stretch films (cling foils) for food [5]. The most commonly used plasticizers are the phthalate di-esters, but there is serious concern that several commonly used phthalates may form small amounts of mono-esters that harm life reproduction systems [6–8]. Therefore there has been a trend to substituting phthalate esters with other less harmful compounds that still do the job as plasticizers. Typical example compounds with these properties are compounds belonging to the family of adipate plasticizers (Fig. 1) that are considered harmless [9]. Alcohols of chain

* Corresponding author. Fax: +45 4525 2412.

E-mail addresses: rwb@kemi.dtu.dk (R.W. Berg),
amalia.dopazo@rai.usc.es (A.D. Otero).

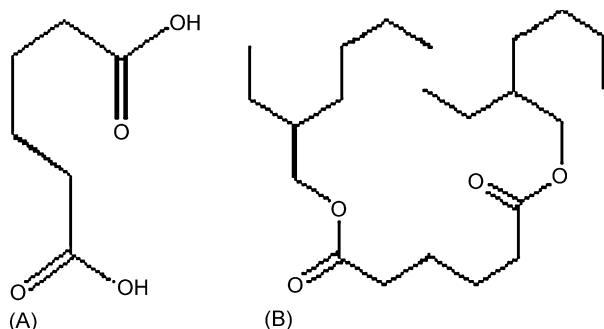


Fig. 1. (A) Adipic acid structure. (B) Structure of di-2-ethylhexyl adipate, also known as DEHA or Adimoll.

lengths similar to those used for phthalate plasticizers can be esterified with adipic acid, rather than phthalic anhydride, to produce the family of adipate ester plasticizers. For example, esterification of 2-ethylhexanol with adipic acid yields di-2-ethylhexyl adipate (DEHA), also known as di-octyl adipate (DOA). Typical commercial adipic acid di-esters (AEs) are based on aliphatic alcohols in the C8–C10 range, because incompatibility problems can be encountered at higher carbon numbers, especially at high addition levels [10]. A list of AEs studied here is given in Table 1.

Adipic acid di-esters (AEs), when used in PVC, in addition to the environmental friendliness, contribute the property of improved low temperature performance, in comparison to phthalates, and significantly lower the viscosity of the plastics, due to the lower inherent viscosity of the plasticizer itself, a useful property in many applications. But it is not so easy to analyse for the AE plasticizers [11].

The aim of this project was to see if Raman spectroscopy can be used to determine the presence of adipate ester plasticizers in commercial flexible PVC products, and if it can detect what kind of ester and how much is present. As Raman literature is nearly nonexistent on these compounds [12], we set out to measure a range of commonly used esters for reference purposes. We have previously shown that the presence of phthalate esters in PVC can be analyzed by Fourier transform (FT-) Raman spectroscopy excited with a 1064 nm deep red laser [1]. Here we report a similar study on the detection of AEs in soft PVC. We have applied FT-Raman spectroscopy to a

range of samples containing adipate esters in pure form as well as in samples of poly vinyl chloride plastics. FT-Raman spectra of 11 AEs are given below. It is demonstrated that the presence of AEs in PVC products could be detected, and by use of proper reference samples quantitative determination of the adipate ester content is possible under certain constraints. It is shown that AEs rather weak spectra in comparison to PVC and that the AEs as a group give cannot be definitively identified by their characteristic Raman bands because other aliphatic dicarboxylic esters have similar bands, limiting the detection possibilities for the kind and amount of ester present in a sample. By use of proper reference samples quantitative determination of the adipate ester content is in principle possible, as it is shown here in one example.

2. Experimental

Spectra were obtained with a Bruker IFS 66 Fourier transform spectrometer with an FRA-106 Raman attachment. The exciting source was a 1064 nm near-infrared Nd-YAG laser with a nominal power of 100 mW. The scattered light was filtered and collected on a liquid N₂ cooled germanium-diode detector, giving a resolution of approximately 2 cm⁻¹ between individual pixels [13]. Stokes Raman spectra were collected in the range from 100 to 3500 cm⁻¹ at approximately 23 °C, with no particular specimen preparation. All mentioned adipate esters (see Table 1) were liquids at 23 °C. The esters were obtained commercially or made in our laboratory by means of a mixture of adipic acid and the corresponding alcohol (1-hexyl, isoamyl, isopropyl). They were measured in small glass test tubes. The samples of plastics, made as described below, were placed directly in the beam. No background subtraction was performed for the spectra.

Plastics samples were made in our laboratory to contain known amounts of powdered PVC (molar weight of approximately 175,000) and a common commercial plasticizer, DEHA. The samples were prepared by thoroughly mixing the PVC with the liquid plasticizer under different conditions of time, temperature and agitation. As a characteristic plasticizer, we have chosen to use Adimoll, di-2-ethylhexyl adipate, or DEHA, CAS No. [103-23-1] from LanXess (Bayer AG, Germany). The different mixtures were placed in small sealed glass containers and given suitable heat treatment conditions (for 6–12 min in an oven at about 120–140 °C) to obtain samples with good homogeneity. Best plastics were achieved in the range of 40–50 wt.% DEHA and with agitation. When the samples were cold, FT-Raman spectra were measured directly through the glass wall of the containers. The adipate ester spectra are obtainable from the authors or other sources [14].

3. Results and discussion

The obtained reference spectra for a number of AEs are shown in Fig. 2. The spectra have been scaled to let the broad CH stretching feature at 2900–3000 cm⁻¹ have about the same size, making the relationship among the spectra readily apparent. It is seen of course that the spectra differ according

Table 1
Studied neat adipate esters: name, CAS-number, formula and source

Diisobutyl adipate, iso-butyl, [141-04-8], C ₁₄ H ₂₆ O ₄ , Sigma–Aldrich
Diisodecyl adipate, iso-decyl, [27178-16-1], C ₂₆ H ₅₀ O ₄ , Sigma–Aldrich
Diamyl adipate, iso-amyl, [14027-78-2], C ₁₆ H ₃₀ O ₄ , own product
Diisopropyl adipate, iso-propyl, [6938-94-9], C ₁₂ H ₂₂ O ₄ , own product
Diisononyl adipate, iso-nonyl, [33703-08-1], C ₂₄ H ₄₆ O ₄ , BASF
Bis(1-butylpentyl) adipate, BBPA, [77916-77-9], C ₂₄ H ₄₆ O ₄ , Sigma–Aldrich
Di-2-ethylhexyl adipate, DEHA, [103-23-1], C ₂₂ H ₄₂ O ₄ , (Adimoll) Bayer (LanXess)
Diethyl adipate, DEA, [141-28-6], C ₁₀ H ₁₈ O ₄ , Sigma–Aldrich
Dimethyl adipate, DMA, [627-93-0], C ₈ H ₁₄ O ₄ , Sigma–Aldrich
Dihexyl adipate, 1-hexyl, [110-33-8], C ₁₈ H ₃₄ O ₄ , own product
Adipic polyester, 1,3-butylene glycol polymer, Ultramoll-III (trade name for a highly viscous plasticizer), [24937-93-7], no formula, from LanXess

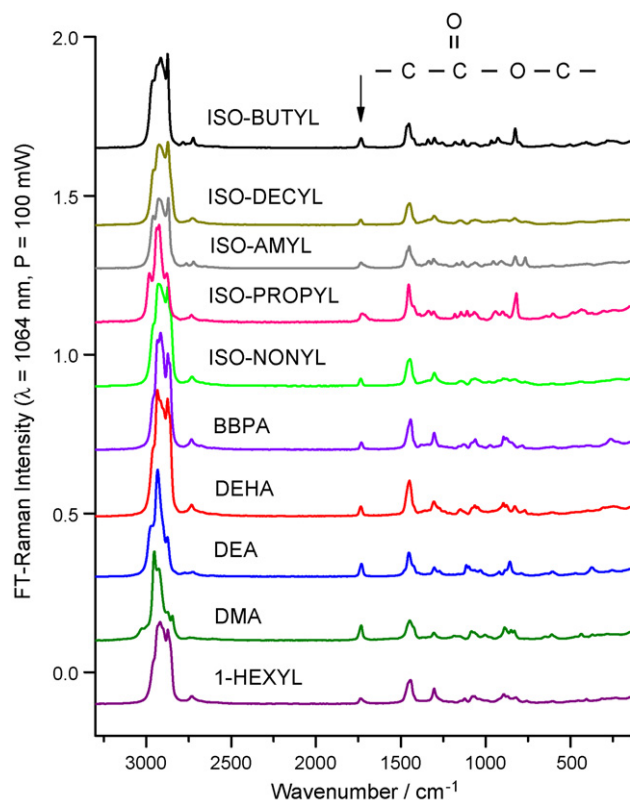


Fig. 2. FT-Raman spectra of adipate esters.

to the kind of alcohol but also have common features. The band at approximately 1734 cm^{-1} occur in all spectra and must be assigned to the $\text{C}=\text{O}$ stretching vibration of the ester group $-\text{C}(\text{C}=\text{O})-\text{O}-\text{C}-$, whereas the peaks at about $2950\text{--}2900$ and 1450 cm^{-1} are due to CH_3 and CH_2 bond stretchings and angle bendings, see e.g. [15].

However, it must be realized that AEs as a group cannot be easily identified by their characteristic Raman $-\text{C}(\text{C}=\text{O})-\text{O}-\text{C}-$ ester group bands because other aliphatic di-carboxylic esters have similar bands. Also, many other carbonyl-containing materials may give rise to a band around 1734 cm^{-1} . Due to

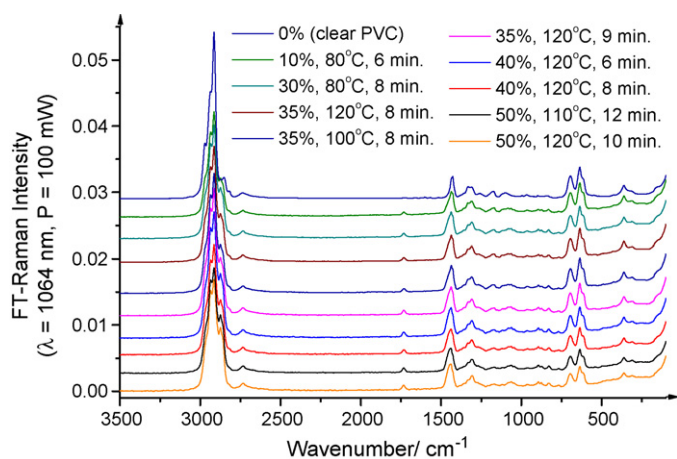


Fig. 3. FT-Raman spectra of PVC samples containing DEHA (Adimoll) in known amounts.

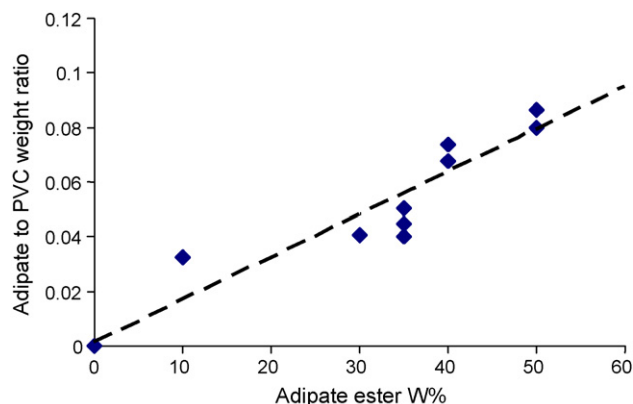


Fig. 4. Graph of adipate-to-PVC area ratio vs. the adipate content (wt.%) in Adimoll softened PVC-samples. A dashed trend line is included. The precision and reproducibility of the results were limited by sample inhomogeneity and problems with estimation of the baseline position.

these spectral similarities, it is doubtful whether it will be possible to determine qualitatively the exact kind of ester (or esters) present in a mixed sample. Furthermore, the AE spectra are rather weak in comparison to PVC. This feature seriously limits the detection of what kind of ester and how much is present in a sample.

Quantitative analysis of AEs: FT-Raman spectra of home made plastics samples, containing known amounts of PVC and Adimoll (DEHA) plasticizer are shown in Fig. 3. The data for the Adimoll signal may be investigated versus the amount known to be present in the sample, in order to see if there is any correlation. By use of an appropriate integration procedure on the FT-Raman spectrum of each sample, the area under the 1734 cm^{-1} peak over the estimated background was determined. The same was done for the PVC peaks at $600\text{--}700\text{ cm}^{-1}$. A graph of the area ratio adipate-to-PVC determined in this way versus the absolute adipate mass content (wt.%) in the sample is shown in Fig. 4. From this standardization curve and the shown trend line, it appears that it should be possible from a single Raman measurement to estimate semi-quantitatively the amount of adipate ester in the soft PVC samples. Also it appears that the area ratios are quite small (y-axis in Fig. 4). It means that the sensitivity of the method is limited. This is probably true in general for adipate ester softened PVC. Furthermore, the method requires it to be known beforehand, that only a particular adipate ester has been applied.

To conclude, by using the ratio of band areas of the two components in the soft plastics, we do not see FT-Raman spectroscopy as an easy way to quantify the amount of AEs in a range of different PVC products.

4. Perspective

When comparing the result of the present study of the adipate esters in PVC to our previous results on phthalate esters in PVC [1], we see an important perspective, however negative the result may seem. FT-Raman spectroscopy may still be interesting as a method for PVC-analysis: one can use the

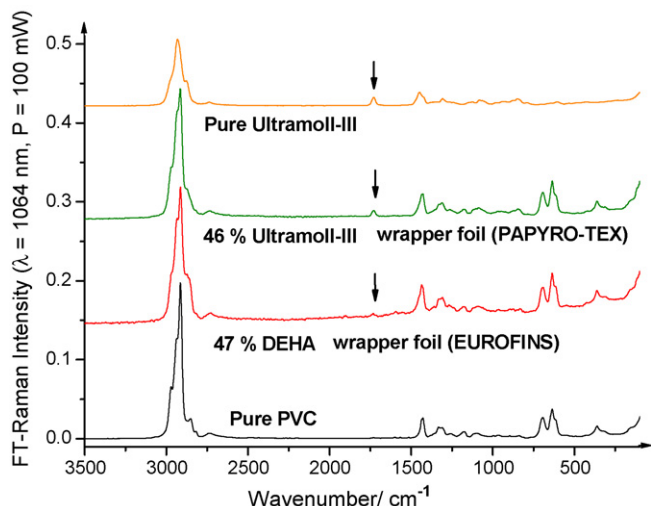


Fig. 5. Raman spectrum of two different PVC foil products and its components. Arrows show the 1734 cm^{-1} band of the $-\text{C}(\text{C}=\text{O})-\text{O}-\text{C}-$ ester groups. Several food cling foil samples from European and American airports did give FT-Raman spectra looking like these foil products, giving evidence of absence of phthalate esters. Spectra have been shifted in y-axis for clarity.

absence of any Raman band in the $1020\text{--}1060\text{ cm}^{-1}$ range of the AEs, as a means to verify that a given soft PVC plastics sample does not contain any significant amount of phthalate esters. This statement is based on the results of our previous study [1], in which we have shown that the phthalate esters gave very strong bands at around 1040 cm^{-1} (due to the phthalate aromatic ring vibrations of the ortho-phenyl group). If a given PVC sample does not have a signal at around 1040 cm^{-1} it cannot contain phthalate esters. But as shown here, it may contain adipate esters. However, it should be noted that the reverse is not true, i.e. bands may occur at around 1040 cm^{-1} in a PVC sample because of other reasons than phthalate ester content. Examples would be benzoic acid esters.

To test these statements we have measured the spectra for a range of different PVC consumer products. The Raman spectra of PVC cling film products of known composition are shown in Fig. 5. The spectra clearly display peaks that can be recognized as due to PVC and adipate esters, respectively (Ultramoll-III is a trade name for a highly viscous adipic polyester plasticizer, see Table 1). In addition to the results in Fig. 5, several food cling foil samples from European and American airport kitchens have been examined to give FT-Raman spectra looking like the spectra in Fig. 5, i.e. with no phthalate ester bands.

5. Conclusions

FT-Raman spectroscopy may be considered a simple and easy technique for fast in situ analysis of PVC samples—with respect to identifying the base-polymer (PVC) as well as giving clues to the nature of the plasticizer. The present work extends the previous work on phthalates [1]. We hope to show that the FT-Raman method may be used for screening of large amounts of consumer products (cling film for food, children's toys [6], etc.) for commonly used plasticizers, although such products are

likely to contain other additives/colorings that may well interfere or mask the bands characteristic of the plasticizer. We have now included adipate di-esters, although they have much less characteristic spectra than phthalate esters, and for PVC softened by a known adipate ester, shown that semi-quantitative determination of the content of the AE plasticizer should be obtainable from a single FT-Raman spectrum after establishing appropriate reference (calibration) data. However the similarities in the spectra of the common di-alkyl adipates limit qualitative determination of the exact kind of ester (or esters) present in a mixed sample, and the sensitivity of the method is limited.

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